

ADSORPTIVE DESULFURIZATION OF DIESEL FUEL OVER A METAL SULFIDE-BASED ADSORBENT

Xiaoliang Ma, Lu Sun, and Chunshan Song*

Clean Fuels and Catalysis Program, The Energy Institute and
Department of Energy and Geo-Environmental Engineering,
The Pennsylvania State University, 209 Academic Projects Building,
University Park, PA 16802
*E-mail: csong@psu.edu

Introduction

Ultra-deep removal of sulfur from diesel fuel is important for environmental protection and fuel cell applications (1,2). The current hydrodesulfurization technology is difficult to reduce the sulfur content in diesel fuel to less than 10 ppmw, because the remaining sulfur compounds in the current commercial diesel fuel are the refractory sulfur compounds, the alkyl dibenzothiophenes with one and/or two alkyl groups at the 4- and/or 6-positions (1,3,4). On the other hand, the conventional hydrodesulfurization technology has to be operated at high temperature and high pressure with hydrogen, resulting in high cost for the ultra-deep hydrodesulfurization. Selective adsorption desulfurization is a promising technology for the ultra-deep desulfurization of diesel fuel. We are exploring a new approach at Penn State called selective adsorption for removing sulfur (PSU-SARS), for ultra-deep removal of sulfur from liquid hydrocarbon fuels (1, 2, 5-11).

The major challenge to our proposed approach is to selectively adsorb sulfur compounds onto the surface of the solid adsorbent but leave the coexisting hydrocarbons including aromatic and olefinic hydrocarbons as well as saturated hydrocarbons, untouched. On the other hand, for the industrial applications one of the key points in the adsorptive desulfurization process is to develop the adsorbent that can be regenerated easily. We envision that the interaction between the sulfur compounds and the adsorption sites on the adsorbent should be selective and suitable in strength. The too strong interaction between them will cause a difficulty in the subsequent regeneration process, while the too weak interaction probably results in a low adsorption selectivity and low capacity. In the present approaches we attempted to develop a metal-sulfide-based adsorbent that not only can selectively adsorb the sulfur compounds but also can be easily regenerated without using hydrogen gas.

Experimental

Two model diesel fuels (MD-1 and MD-2) were used in the present study. MD-1 contains the same molar concentration (3.9 mmol/L) of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and dimethyldibenzothiophene (4,6-DMDBT), and 1-methylnaphthalene (1-MNA). MD-2 contains only one sulfur compound, DBT. The total sulfur concentration in MD-1 and MD-2 is 486 and 200 ppmw, respectively. MD-1 and MD-2 also contain 10 wt% of n-butylbenzene for mimicking the aromatics in the real diesel. The detailed composition of the model diesel fuels is listed in Table 1 and 2. The sulfur compounds and hydrocarbons contained in the fuels were purchased from Aldrich without further treatment before use.

The adsorbent used in the present study was Adsorbent-6, which was prepared from CoMo oxides supported on γ -alumina (CoMo/ γ -Al₂O₃; CoO: 3wt%; MoO₃: 14wt%; Surface area: 183 m²/g; Pore volume: 0.4755 ml/g; Average pore size: 102 Å). CoMo/ γ -Al₂O₃ was sulfided at 350 °C with 10 vol % H₂S in H₂ at a flow rate of 200 ml/min for 4 h. The sulfided CoMo/ γ -Al₂O₃ was cooled to room temperature under the same atmosphere, and then, kept into hexane before use. Adsorbent-6 was obtained by treating the sulfide CoMo/ γ -Al₂O₃ with H₂ at 300 °C for 60 min. About 2 g of the sulfided

CoMo/ γ -Al₂O₃ was parked into a stainless steel column with internal diameter of 4.6 mm and length of 150 mm. The adsorbent bed volume was 2.49 ml. H₂ gas was passed through the column at ambient pressure and a flow rate of 20 ml/min. After the treatment, the column temperature was reduced to the assigned temperatures for the adsorption.

The adsorption experiments were performed at ambient pressure without using H₂ gas. The model diesel fuel was fed into the column and flowed up through the adsorption bed. The flow rate was 0.2 ml/min, corresponding to a LHSV of 4.8 h⁻¹. The treated model fuel was collected for analysis. The regeneration of the spent adsorbents was accomplished by washing the adsorbent with a polar solvent followed by heating the adsorbent to remove the remaining solvent. The polar solvent was pumped through the adsorbent bed at 60 °C and a LHSV of 4.8 h⁻¹. After washing, the adsorbent bed was heated to 300 °C under a nitrogen flow at 20 ml/min for 1 h, and then, was cooled to the assigned temperature for the subsequent adsorptive desulfurization.

Analysis of concentration of sulfur compounds in the treated MD-1 was performed by using GC with a capillary column, XTI-5 (Restek) 30 m x 0.25 mm x 0.25 μ m, and a flame ionization detector (FID). An Antek 9000 Series Sulfur Analyzer (detection limit 0.5 ppmw) was used for determining sulfur concentration in the treated MD-2.

Results and Discussion

Figure 1 shows the molar concentration of sulfur compounds and 1-MNA at the outlet as a function of the effluent amount for the adsorptive desulfurization of MD-1 over Adsorbent-6 at 50 °C. The first break-through compound was 1-MNA with a break-through point at 0.2 g/g (gram of MD-1 per gram of adsorbent) and a saturation point at 1.6 g/g. The second one was 4,6-DMDBT with a break-through point at 0.4 g/g. The concentration of 4,6-DMDBT was kept below 0.2 mmol/l before the effluent amount reached 2.5 g/g, and then, increased quickly to the saturation point at 4.4 g/g. Break-through point of 4-MDBT was at 2.5 g/g with a saturation point at 5.0 g/g. The last break-through compound was DBT with a break-through point at 3.5 g/g and a saturation point at > 5.5 g/g. It is clear that Adsorbent-6 has much higher selectivity to adsorb DBTs compared to aromatics represented by 1-MNA. As is well known, 1-MNA has a higher π -electron density on its aromatic ring than that of DBTs (9), although the aromatic ring size of the former is smaller than that of the latter. It is clear that interaction between the S atom and the adsorption sites plays an important role in the competitive adsorption between DBTs and 1-MNA. From a comparison of DBT, 4-MDBT and 4,6-DMDBT, the adsorption selectivity increases in the order of 4,6-DMDBT < 4-MDBT < DBT, implying that the methyl groups at the 4 and 6-positions inhibit the interaction between the S atom and the adsorptive sites on the adsorbent, which results in the decrease in the adsorption capacities of 4,6-DMDBT and 4-MDBT.

It should be noted the system we used is based on selective adsorption, not reaction. No detectable biphenyls and cyclohexylbenzenes type products were found in the effluent, indicating that no HDS reaction takes place at such conditions.

Adsorption desulfurization of MD-2 over Adsorbent-6 was conducted at 50 °C under ambient pressure. The total sulfur concentration at outlet as a function of the treated MD-2 amount is shown in Figure 2. When the treated MD-2 amount was less than 2.5 g/g, the sulfur concentration at outlet was less than 10 ppmw. After 2.5 g/g of the effluent amount, the sulfur concentration increased sharply with increasing the effluent amount. Adsorbent-6 was saturated when the effluent amount reached about 8 g/g. The adsorptive capacity corresponding to the break-through point at 10 ppmw sulfur level and the saturation point was 0.65 and 0.77

milligram of sulfur per gram of adsorbent (mg-S/g-A), respectively. Adsorption desulfurization of MD-2 over Adsorbent-6 at 150 °C was also conducted, but the performance was poorer than that at 50 °C. This indicates that lower temperature is better for the adsorptive desulfurization over this type of adsorbents, in contrast to the nickel-based adsorbents (12).

After regeneration of the spent adsorbent, the adsorption performance of the regenerated adsorbents was tested. The adsorption break-through curves for the regenerated adsorbents are shown in Figure 2 in comparison with the curve for the fresh adsorbent. It shows clearly that the break-through curves for the 1st regenerated adsorbent and the 2nd regenerated adsorbent coincide well with that for the fresh adsorbent, especially when the treated MD-2 amount is less than 4 g/g. The adsorption capacity corresponding the break-through point at 10 ppmw sulfur level for the 1st regenerated adsorbent and the 2nd regenerated adsorbent is 0.65 and 0.66 mg-S/g-A, respectively. It implies that the spent adsorbent can be regenerable, and almost all adsorption capacity in the adsorbent can be recovered by our developed method.

Acknowledgments. We gratefully acknowledge the financial support by US Department of Energy and US Department of Defense.

References

1. Song, C., Ma, X., Appl. Catal. B., 41 (1-2), 207-238 (2003).
2. Song, C. *Catalysis Today*, 77 (1), 17-50 (2002).
3. Ma, X., Sakanishi, K., Mochida, I., Ind. Eng. Chem. Res. 33, 218 (1994).
4. Gates, B.C., Topsoe, H., Polyhedron 16, 3213 (1997).
5. Ma, X., Sun, L., and Song, C., *Catal. Today*, 77, 107-116 (2002).
6. Velu, S., Ma, X., and Song, C., *Am. Chem. Soc. Div. Petr. Chem. Prepr.*, 48 (2), 58-59 (2003).
7. Velu, S., Watanabe, S., Ma, X., and Song, C., *Am. Chem. Soc. Div. Petr. Chem. Prepr.*, 48 (2), 56-57 (2003).
8. Ma, X., Sprague, M., Sun, L., and Song, C., Ultra-Deep Desulfurization of Gasoline and Diesel for Fuel Cell Applications by SARS Adsorbent and Process. Materials Research Society Fall 2002 National Meeting, Boston, Dec. 2-6, 2002
9. Ma, X., Sprague, M., Sun, L., and Song, C., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 47, 452 (2002).
10. Velu, S., Ma, X., and Song, C., Zeolite-Based Adsorbents for Desulfurization of Jet Fuel by Selective Adsorption. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 47, 457 (2002).
11. Ma, X., Sun, L., Yin, Z. and Song, C., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 46 (2), 648-649 (2001).
12. Ma, X., Velu, S., Sun, L., and Song, C., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 48, (2003), in submission.

Table 1 Composition of MD-1

No.	Name	Concentration		
		wt %	mmol/l	ppmw
Sulfur compounds				
1	DBT	0.095	3.93	165
2	4-MDBT	0.099	3.81	160
3	4,6-DMDBT	0.107	3.85	162
Total Sulfur			11.59	486
4	Naphthalene (99%)	0.067		
5	2-methylnaphthalene (98%)	0.074	3.85	
6	n-Hexadecane(99+%)	39.97		
7	n-Dodecane(99+%)	39.50		
8	n-Tetradecane (99+%)	0.109		
9	Decalin(99+%)	9.988		
10	t-Butylbenzene(99%)	9.988		

Table 2 Composition of MD-2

No.	Name	Concentration		
		wt %	mmol/l	ppmw
1	DBT (99+%)	0.115	4.84	200
2	1-Methylnaphthalene(97%)	0.090	4.89	
3	n-Hexadecane(99+%)	88.67		
4	n-Tetradecane (99+%)	0.122		
5	n-Butylbenzene(99%)	10.01		
Others		1.00		

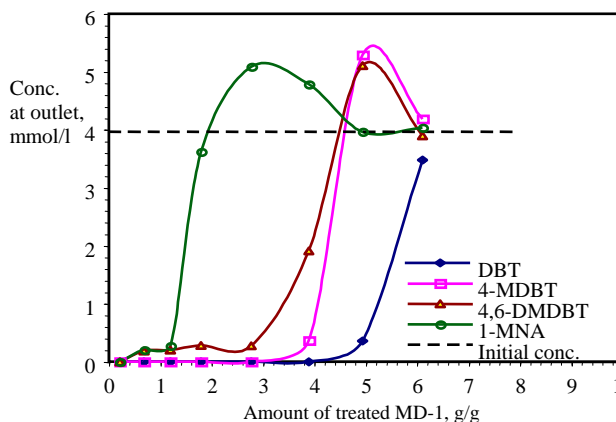


Figure 1. Break-through curves of MD-1 over Adsorbent-6

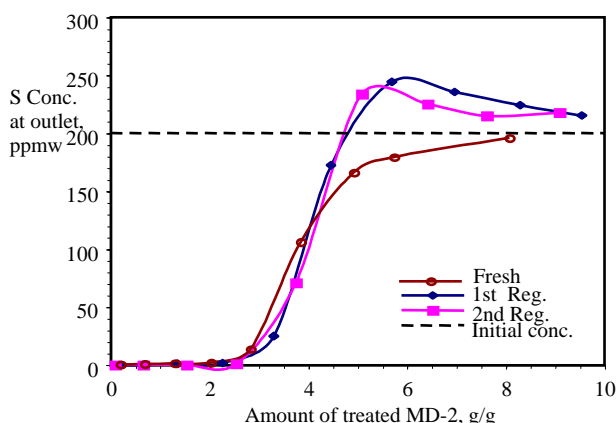


Figure 2. Break-through curves of MD-2 over fresh and regenerated adsorbents at 50°C